

coefficient are both much greater than for a diffusion controlled current. A mechanism is proposed for this wave which is based on the catalysis

of hydrogen discharge by the  $\text{Re}^{-1}\text{-Re}^{+1}$  couple.

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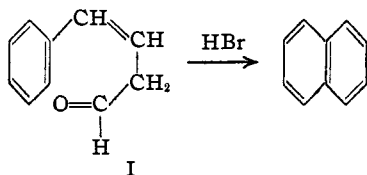
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## NOTES

### Cyclization of $\beta$ -Styrylacetaldehyde

BY CHARLES K. BRADSHER<sup>1</sup>

It has been reported by Rinkes<sup>2</sup> that  $\beta$ -styrylacetaldehyde (I) may be cyclized to give naphthalene. Inasmuch as he failed to report either the



yield or the method employed in this cyclization, we have undertaken to reinvestigate this matter.

The required aldehyde (I) was prepared by the more convenient method of Meyer,<sup>3</sup> involving the pyrolysis of  $\alpha$ -methoxycinnamylacetic acid. When refluxed with hydrobromic and acetic acids, the aldehyde gave naphthalene in 25% yield.

While this is the simplest case of aromatic cyclodehydration to give a naphthalene nucleus, there are a number of other instances in which a cyclization of this type is believed or known to take place.<sup>4</sup>

### Experimental

**Naphthalene.**— $\beta$ -Styrylacetaldehyde was prepared in 25% yield by the method of Meyer.<sup>3</sup> This aldehyde (0.65 g.) was dissolved in acetic acid (13 cc.) and added dropwise to boiling 34% hydrobromic acid (6.5 cc.), the addition requiring about five hours. Refluxing was allowed to continue for a total of forty-eight hours. The mixture was then diluted with water and extracted with ether. The ethereal extract was washed, dried, concentrated and the residue sublimed *in vacuo*. The sublimate consisted of small white plates; m. p. 80–81°; yield, 0.14 g. (25%). This material showed no depression of melting point when mixed with an authentic sample of naphthalene.

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RECEIVED NOVEMBER 10, 1941

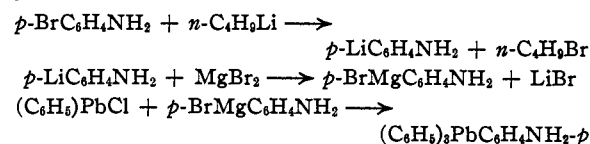
- (1) National Research Fellow (participating basis).
- (2) Rinkes, *Rec. trav. chim.*, **39**, 200 (1920).
- (3) Meyer, *Compt. rend.*, **204**, 508 (1937).
- (4) E. g. Zincke, *Ann.*, **240**, 137 (1887); Erlenmeyer and Kunlin, *Ber.*, **35**, 384 (1902); Haworth and Sheldrick, *J. Chem. Soc.*, 636, 1576 (1935); Omaki, *J. Pharm. Soc. Japan*, **58**, 4 (1938).

### Diazotization of an Aminoaryllead Compound<sup>1</sup>

BY HENRY GILMAN AND C. G. STUCKWISCH

*p*-Aminophenyllithium has been used for the introduction of the *p*-aminophenyl group into organoarsenic and organophosphorus compounds.<sup>2</sup> In attempts to effect a related transformation between triphenyllead chloride and *p*-aminophenyllithium, complex mixtures were obtained. The difficulty probably resides in the metal-metal interconversion reactions between organolead and organolithium compounds.<sup>3</sup>

However, because M–M interconversions only occur to a highly subordinated extent between Grignard reagents and organolead compounds, we first converted the RLi compound to the corresponding RMgBr compound by means of magnesium bromide.<sup>4</sup> The following sequence of reactions illustrates the preparation of triphenyl-*p*-aminophenyllead, which was obtained in a 66% yield.



The *p*-aminophenyllead compound was diazotized by conventional procedures, despite the presence in the molecule of a supposed labilizing aminoaryl group. The diazonium compound was coupled with  $\beta$ -naphthol to give an azo-lead compound which was red in acid solution and green in basic solution. The general reactions described now provide the essential means for the resolution of some RM compounds, and the introduction of water-solubilizing groups to vary the lipid-water distribution of the less chemically reactive RM compounds.

- (1) Paper XLIV in the series "Relative Reactivities of Organo-metallic Compounds"; the preceding paper is in THIS JOURNAL, **63**, 2844 (1941).
- (2) Gilman and Stuckwisch, *ibid.*, **63**, 2844 (1941).
- (3) Gilman and Moore, *ibid.*, **62**, 3206 (1940).
- (4) Gilman and Kirby, *ibid.*, **63**, 2046 (1941).

### Experimental

**Triphenyl-*p*-aminophenyllead.**—To 0.128 mole of *n*-butyllithium in 200 ml. of ether was added dropwise 6.9 g. (0.04 mole) of *p*-bromoaniline in 50 ml. of ether. After addition was completed, the solution was stirred at room temperature for thirty minutes. The low temperature ( $-60^{\circ}$ ) reported previously<sup>2</sup> for the preparation of *p*-aminophenyllithium is not necessary. A slight excess of an ether solution of anhydrous magnesium bromide, prepared by adding bromine dropwise to magnesium suspended in ether, was then added to the reaction mixture. The Grignard reagent thus formed was allowed to react with 18.4 g. (0.04 mole) of triphenyllead chloride for two hours at room temperature, and then hydrolyzed with iced ammonium chloride solution.

The ether layer was extracted with dilute hydrochloric acid. From the hydrochloric acid extract was isolated 3.5 g. of *p*-bromoaniline. The residual ether layer was dried and then evaporated under reduced pressure. The solid residue yielded, after several crystallizations from petroleum ether (b. p. 60–68°), 2.2 g. of a white crystalline solid, m. p. 166–167°.

The ether insoluble material obtained from the reaction was extracted with three 200-ml. portions of petroleum ether (b. p. 60–68°). The extractions yielded 4.8 g. of material melting at 166–167° and identical with the substance obtained from the ether soluble portion. The total yield was 7.0 g. or 66%, assuming that the unrecovered *p*-bromoaniline was converted to *p*-aminophenyllithium.

*Anal.* Calcd. for  $C_{24}H_{21}NPb$ : Pb, 39.01. Found: Pb, 39.45.

**Triphenyl-1-(2-hydroxynaphthyl)-azophenyl-4-lead.**—One gram of triphenyl-*p*-aminophenyllead was diazotized and coupled with  $\beta$ -naphthol in the usual manner. The coupling product, crystallized from dilute ethanol, decomposed at 135°, and was red in acid solution and green in the presence of base.

*Anal.* Calcd. for  $C_{34}H_{26}ON_2Pb$ : Pb, 30.02. Found: Pb, 29.65.

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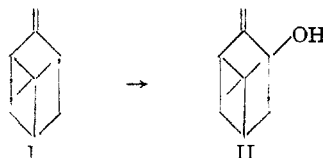
RECEIVED JANUARY 22, 1942

### The Oxidation of $\beta$ -Pinene with Selenium Dioxide

BY LLOYD M. JOSHEL AND S. PALKIN

The oxidation of  $\beta$ -pinene (I) with selenium dioxide<sup>1,2</sup> has been recently reinvestigated by Stallcup and Hawkins,<sup>3</sup> who reported that no pinocarveol (II) or other alcohol could be found in the oxidation mixture. In order to make available a ready means for the preparation of pinocarveol from  $\beta$ -pinene and in view of the possible bearing on the mechanism of selenium dioxide oxidation, we are prompted to report the results of

some experiments made some time ago in this Laboratory.



Both the French workers<sup>1</sup> and Stallcup and Hawkins<sup>3</sup> used one mole (two equivalents) of selenium dioxide per mole of  $\beta$ -pinene. We found that when somewhat less than one-half a mole of selenium dioxide is used per mole of  $\beta$ -pinene, pinocarveol is readily obtained. Zacharewicz,<sup>2</sup> who used an even smaller ratio of selenium dioxide to  $\beta$ -pinene, also obtained pinocarveol but in less than one-half the yield reported below.

We are indebted to Messrs. Hawkins and Stallcup for their kindness in trying out the oxidation procedure described below. In a private communication Dr. Hawkins has informed us that they have confirmed our findings with regard to the main product, pinocarveol, and the small amount of carvopinone formed under these conditions.

### Experimental

A solution of 21 g. (0.16 mole) of c. p. selenious acid in 40 ml. of absolute ethanol was added dropwise during one-half hour, with mechanical stirring, to 54 g. (0.40 mole) of  $\beta$ -pinene. During the addition the solution became warm and turned yellow in color. After stirring another half-hour at room temperature, the solution was refluxed for four hours. The solution, which was red at this point, was then steam-distilled and the oil in the distillate was taken up in ether, washed, dried and distilled under nitrogen, furnishing, along with other fractions, 21 g. (42%) of a colorless liquid, b. p. 101.5–103° (25 mm.). The physical constants and active hydrogen determination indicated that this material was pinocarveol of about 85–90% purity. It could be further purified by conversion to the borate. The alcohol was heated with an equal volume of ethyl borate at 100–125° for one-half hour and the volatile contaminants removed by reducing the pressure gradually to 2 mm. while the bath was raised to 150°. The residual ester was then simultaneously hydrolyzed and steam distilled and the oil in the distillate taken up in ether, washed, dried, and distilled under nitrogen. In this way a colorless liquid, b. p. 101–102° (20 mm.), was obtained in 69% yield from the crude alcohol, or 29% over-all yield;  $n_D^{21}$  1.4995,  $d_4^{20}$  0.9798,  $\alpha_D^{20}$  +67.48°,  $\alpha_D^{20}$  +71.57°,  $\alpha_D^{20}$  +83.37°. Active hydrogen determination (semimicro) with methylmagnesium iodide showed 11.55% hydroxyl; calcd., 11.17%. The phenylurethan melted at 84–86°. This compares favorably with the m. p. of this derivative as usually reported,<sup>3,4</sup> although Schmidt<sup>5</sup> reported that on

(1) Dupont, Allard and Dulou, *Bull. soc. chim.*, [4] **63**, 599 (1933).

(2) Zacharewicz, *Roczniki Chem.*, **17**, 630 (1937).

(3) Stallcup and Hawkins, *THIS JOURNAL*, **63**, 3339 (1941).

(4) Schmidt, *Ber.*, **62**, 2945 (1929).

(5) Schmidt, *ibid.*, **63**, 1129 (1930).